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Chemical Engineering Division

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TABLE OF CONTENTS

LIST OF FIGURES

TABLE

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$$\log P_U = (5.677 \pm 0.273) - (25898 \pm 192)/T,$$

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and

$$\log P_{P_2} = (10.319 \pm 1.203) - (38454 \pm 1480)/T.$$

A value for the enthalpy of sublimation of uranium at 298°K was found to be 129.0 ± 3.7 kcal/mole from averaging our second- and third-law values, which were in good agreement with each other.

I. INTRODUCTION

A mass-spectrometric Knudsen effusion investigation of uranium monophosphide (UP) has been carried out in the range 2073-2423°K. Since the monophosphide preferentially vaporized phosphorus and formed the two-phase system $U(\ell)-UP_{1-x}(s)$, the basic thermodynamic properties reported in this report are the partial pressures in equilibrium with this two-phase system.

Uranium monophosphide has a potential as a nuclear fuel, and its stability at high temperatures has been demonstrated in several studies, particularly in the first of two reported mass-spectrometric effusion studies by Gingerich and Lee.[1,2] However, Ref. 1 appears inconclusive for the

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More recent work in the literature has confirmed that uranium monophosphide becomes hypostoichiometric on vaporization in vacuum, and there is some concrete evidence that strongly implies that it shifts continuously toward more uranium-rich compositions, finally precipitating out the liquid-uranium phase. Thus, Baskin[3] has reported the preferential vaporization of phosphorus in vacuum between 1673 and 2473°K and found that the product was hypostoichiometric. Allbutt et al.[4] reported that vacuum sintering of the monophosphide above 2073°K led to a preferential loss of phosphorus and the formation of a liquid-uranium phase.

Third, although Gingerich and Lee,[1] in treating their vapor-pressure data, adopted the assumption that UP vaporized congruently over the temperature range of investigation, their partial-pressure data argue against the validity of the assumption when the data are used to calculate the composition of the gas phase. Thus, at ~2000°K, Gingerich and Lee report equal partial pressures for the U and P species and approximately one-fourth these values for the P_2 species. By appropriately combining the effusion equations, one can calculate that, using their pressures, the composition of the effusing gas in P/U atom ratio units would have been ~3.8. Quite obviously, the solid phase would be in the process of becoming uranium-rich during their measurements. Since the hypostoichiometric range appears to be small (0.00 to ~0.04 unit of x in UP_{1-x} at about 2173°K),[5] vaporization would probably soon lead to rejection of the liquid-uranium phase. Gingerich and Lee[1] noted the tendency toward deviation from stoichiometry, as evidenced by "...a slight decrease in total vapor pressure and in the P_P/P_U ratio as vaporization proceeded... ." They did not observe the presence of a uranium phase in the residues that were examined, however.

The present mass-spectrometric effusion investigation was undertaken to resolve some of the conflicts in the accumulated data so that more confidence can be placed on the thermodynamics and stability evaluations of uranium monophosphide.

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The present mass-spectrometric effusion investigation was undertaken to resolve some of the conflicts in the accumulated data so that more confidence can be placed on the thermodynamics and stability evaluations of uranium monophosphide.

II. EXPERIMENTAL METHODS

The mass spectrometer used in this research was a Bendix Model 12-107 time-of-flight instrument operated in the pulsed mode.[6] In this mode of operation, the sensitivity of the instrument is approximately 10^{-9} atm. The practical working mass resolution of the instrument for parent ion species is approximately 1 in 250. The studies were performed using tungsten Knudsen cells, with orifice areas $(8.1 \text{ or } 2.0) \times 10^{-3}\ cm^2$, heated by electron bombardment in a high-temperature effusion assembly modeled after that by Rauh et al.[7]

Temperatures were read with a Leeds and Northrup disappearing-filament optical pyrometer by sighting directly into the orifice of the effusion cell and correcting for the absorbence of the sight glass on the mass spectrometer. The pyrometer filament current was calibrated at the freezing point of pyrometric-standard copper. The calibration of the pyrometer scales at higher temperatures was achieved with tungsten strip bulbs standardized by the National Bureau of Standards. In addition, the pyrometer was compared with another pyrometer which had been calibrated by the rotating-sector method. This comparison showed agreement between the two pyrometers to within 1° at the melting point of platinum.

The uranium monophosphide used was prepared by Baskin and Shalek.[8] Chemical analyses of the material, following the procedures by Milner et al.,[9] showed 88.04% uranium (theoretical: 88.49%), 11.30% phosphorus (theoretical: 11.51%), and 0.27% oxygen. Based on these analyses, the P/U atom ratio of the material was 0.98 ± 0.02. Metallographic analysis showed that the oxygen impurity was present as trace amounts of a UO_2 phase. A careful search yielded no evidence of a uranium metal phase. X-ray analysis indicated only UP with a lattice parameter of $a_0 = 5.589 \pm 0.001$ Å.

Tungsten was chosen as the container material for the effusion studies, since the available evidence indicated it remained essentially inert to uranium monophosphide up to 2473°K.[10]

When stoichiometric uranium monophosphide was initially heated to between 2073 and 2423°K, the ion species observed mass-spectrometrically (using an ionizing electron energy of 30 eV) were U^+, P^+, P_2^+, P_4^+, UO^+, and UO_2^+. The UP^+ species reported in the most recent work of Gingerich[2] was not observed because the intensity of the ion was below the sensitivity limit of our mass spectrometer. The UO(g) and UO_2(g) species arose from the oxygen contamination of the starting material. A survey of the top of the Knudsen cell and the adjoining heat shields, by means of a movable shutter, showed that essentially all the U(g) came from the orifice, but that all the P_4(g) and part of the P_2(g) and P(g) arose from revaporization (at relatively low temperatures) of phosphorus which had condensed on heat shields above the effusion cell. Thus, in the first case, there was no cause to suspect that

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An investigation of the dependence of the intensities of U^+, P^+, and P_2^+ with the ionizing electron energy showed that all three species were parent species. Appearance potentials were evaluated by the linear-extrapolation method using mercury to calibrate the ionizing-electron voltage scale. Values for the three species were determined to be 4.7 ± 0.5, 10.9 ± 0.5, and 10.3 ± 0.5 eV, respectively. Previous values reported for the appearance potential of U(g) have ranged from 4.7 to 6.25 eV,[11-15] and for P(g), 10.977 eV.[16] Fragmentation of the P_4(g) and P_2(g) species was found to become quite prominent (contributing perhaps 50% of the P^+ observed) at ionizing-electron energies above 18 eV. To avoid this fragmentation, an electron energy of 13 eV was normally used in our experiments.

When a 1-g sample of starting material was heated at 2309°K in 3-hr intervals for 15 hr, the ion intensities of U^+, P^+, and P_2^+ became constant after 8 hr at temperature. During this 8-hr period, the partial pressure of U(g) increased by a factor of two and the partial pressures of P(g) and P_2(g) decreased by factors of two and four, respectively. The partial pressures of UO(g) and UO_2(g) decreased by factors of 25 and 200, respectively, demonstrating the preferential vaporization of the UO_2 impurity, as was reported by Baskin.[17] As a general procedure, therefore, to clean up the starting material, all samples were given a preheat treatment in the mass spectrometer until the ion intensity ratio of U^+/UO^+ was ≥ 30. (Typically, this required 1 hr at 2373°K for a 0.2-0.4-g sample.)

III. EXPERIMENTAL RESULTS

The observed increase in the partial pressure of U(g) and concomitant decrease in the partial pressures of P(g) and P_2(g) during effusion in the run discussed above agrees with the observation of Gingerich and Lee[1] and is evidence that the monophosphide phase was tending to become richer in uranium and, therefore, tending to become hypostoichiometric with respect to phosphorus. That the composition of the solid had changed was confirmed by metallographic analysis of portions of the residues from each successive 3-hr heating period. The analysis of quenched* samples after the 3- and 6-hr periods at temperature revealed UP as the major phase, with UO_2 as a minor phase. After 9 hr at temperature, analyses revealed the presence of uranium as an additional minor phase, located at the UP grain boundaries. The nonuniformity of the distribution of the uranium around the grain boundaries indicated that the uranium existed as a second phase at temperature. Considering the quench rate of the samples, had the uranium precipitated

*Cooled by turning off the power to the electron-emitting filament, cooling from 2270 to 1073°K in 1 min.

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*Cooled by turning off the power to the electron-emitting filament, cooling from 2270 to 1673°K in 1 min.

from hypostoichiometric uranium phosphide upon cooling, it would probably have been more uniformly distributed around the UP grains. This nonuniformity in the distribution of the uranium phase among the UP grain boundaries was also observed by Allbutt et al.[4] and cited as evidence for the presence of liquid uranium at temperature. It was also noted in our metallographs that the uranium phase of the quenched samples contained 5-11 wt % tungsten.[18] (The authors of Ref. 18 found the solubility of tungsten in liquid uranium to be 5.8 at. % at 2273°K, corresponding to 7.5 wt % tungsten.)

X-ray diffraction analyses of quenched* samples following vaporization showed that the lattice parameter of the UP was always unchanged from its original value of $a_0 = 5.589 \pm 0.001$ Å. This disagrees with the results of Baskin,[3] who found a decrease in the parameter from $a_0 = 5.589$ Å to 5.583 Å, as the stoichiometry of the monophosphide decreased from 1.00 to 0.97. The reason for this disagreement, at present unknown, appears to be complex, possibly involving different cooling rates, effects of tungsten impurities, and/or the physical state (powder or pellet) of the starting material.

The partial vapor pressures of U(g), P(g), and P_2(g) over the two-phase system $U(\ell)$-$UP_{1-x}(s)$ were determined as a function of temperature from measurements of the U^+, P^+, and P_2^+ ion currents in four separate experiments. The calibration to convert ion intensities to partial pressures was obtained by the rate-of-mass-loss method. That the condensed materials in these experiments did correspond to the two-phase system was determined metallographically or mass-spectrometrically. The latter was accomplished by heating a disk of starting material at a constant temperature until the intensities of the three ionic species were constant with time, and then adding a small pellet of uranium to the disk and again heating to the same temperature. The intensity of the U^+ species was equal to its intensity observed before the uranium charge had been added and did not vary with time. This equivalency established that, during effusion, the starting material had indeed shifted composition to become the two-phase system even before addition of the uranium pellet. The P/U atom ratio of the solid was initially 0.98 ± 0.02 and 0.95 ± 0.02 at the end of the experiment, as determined by chemical analysis. Since excess uranium was present in the residue, the ratio r_s at the phase boundary is $0.98 > r_s > 0.95$, or approximately 0.965 ± 0.02, which compares well with the 0.96 value at 2137°K, as communicated to us by Bowman.[5]

The partial pressure of an effusing species, P_i, is related to its ion current, I_i, and its mass rate of Knudsen effusion, Q_i, by

$$I_i T = C\sigma_i\gamma_i P_i = C\sigma_i\gamma_i Q_i \sqrt{\frac{2\pi RT}{M_i}}, \qquad (1)$$

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*Ibid., see p. 7.

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The partial pressure of an effusing species, P_i, is related to its ion current, I_i, and its mass rate of Knudsen effusion, Q_i, by

$$I_i T = C_0 \gamma_i \sigma_i P_i = C_0 \gamma_i \sigma_i Q_i \sqrt{\frac{2\pi R T}{M_i}} \tag{1}$$

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*Ibid., see p. 7.

where T is the absolute temperature, C is a constant characteristic of the electronics and geometry of the mass spectrometer, σ_i is the ionization cross section, γ_i is the multiplier efficiency, and M_i is the molecular weight. The partial pressures were evaluated[19] from three measurements at a constant temperature (2309°K) of the total mass evaporated in a given time and the intensity of each main ion species integrated as a function of time. Then the observed total mass rate of effusion, Q_T, was partitioned into that due to each of the three principal species by use of the ratios of Eq. 1 with the necessary coefficients estimated as follows. Otvos-Stevenson[20] ionization cross sections were used ($\sigma_U = 55.7$, $\sigma_P = 13.8$, and $\sigma_{P_2} = 27.6$), and multiplier efficiencies were estimated on the assumption[22] that ions of equal velocity have equal multiplier efficiencies; i.e., $\gamma_1/\gamma_2 = (M_2/M_1)^{1/2}$, where M is the molecular weight. When it was necessary to correct evaporation rates for the presence of UO(g) and UO_2(g), the assumption that $\sigma_U = \sigma_{UO} = \sigma_{UO_2}$ was used. This assumption was evaluated to be satisfactory in the studies on the U-UO_2 system.[22] From the three measurements of the rate of mass loss at 2309°K from the U(ℓ)-UP_{1-x}(s) system, the average weight loss through an orifice of 0.101-cm diameter was at the rate of 2.02 mg/(min)(cm^2). Since a linear extrapolation to this temperature of the data obtained between 1823 and 2174°K from the Langmuir evaporation experiments by Allbutt et al.[4] gave an evaporation rate that was within a factor of two (higher) of our value, there appears to be no indication for a vaporization coefficient significantly different from unity.

The partial pressures of U(g), P(g), and P_2(g) were calculated to be 2.89×10^{-6}, 1.89×10^{-6}, and 4.62×10^{-7} atm, respectively, at 2309°K. The equations for the temperature dependencies of the three partial pressures in atmospheres are

$$\log P_U = (5.677 \pm 0.273) - (25898 \pm 192)/T, \tag{2}$$

$$\log P_P = (8.062 \pm 0.240) - (31831 \pm 340)/T, \tag{3}$$

and

$$\log P_{P_2} = (10.319 \pm 1.203) - (38454 \pm 1480)/T \tag{4}$$

from the four series of ion-current measurements, mentioned previously, which had been combined by normalizing the data to a common basis at the midrange temperature. These equations are considered valid in the range 2073-2423°K. From the uncertainty in the experimental data alone, the partial pressures of U(g), P(g), and P_2(g) are known (at a 95% confidence level, 2σ) to within 18, 20, and 44%, respectively. However, it is generally assumed that uncertainties in the ionization cross sections and multiplier efficiencies could be a factor of two. Figure 1 shows the lines representing the above pressure equations, one set of the experimental data (the uranium data is given in Table I, Series A), and, for comparison, the equations reported by Gingerich and Lee[1] from their similar mass-spectrometric where T is the absolute temperature, C is a constant characteristic of the electronics and geometry of the mass spectrometer, σ_i is the ionization cross section, γ_i is the multiplier efficiency, and M_i is the molecular weight. The partial pressures were evaluated[19] from three measurements at a constant temperature (2309°K) of the total mass evaporated in a given time and the intensity of each main ion species integrated as a function of time. Then the observed total mass rate of effusion, Q_T, was partitioned into that due to each of the three principal species by use of the ratios of Eq. 1 with the necessary coefficients estimated as follows. Otvos-Stevenson[20] ionization cross sections were used (σ_U = 55.7, σ_P = 13.6, and σ_{P_2} = 27.6), and multiplier efficiencies were estimated on the assumption[21] that ions of equal velocity have equal multiplier efficiencies, i.e., $\gamma_1/\gamma_2 = (M_2/M_1)^{1/2}$, where M is the molecular weight. When it was necessary to correct evaporation rates for the presence of UO(g) and UO_2(g), the assumption that $\sigma_U = \sigma_{UO} = \sigma_{UO_2}$ was used. This assumption was evaluated to be satisfactory in the studies on the U-UO_2 system.[22] From the three measurements of the rate of mass loss at 2309°K from the U(ℓ)-UP_{1-x}(s) system, the average weight loss through an orifice of 0.101-cm diameter was at the rate of 2.02 mg/(min)(cm^2). Since a linear extrapolation to this temperature of the data obtained between 1825 and 2174°K from the Langmuir evaporation experiments by Alibutt et al.[4] gave an evaporation rate that was within a factor of two (higher) of our value, there appears to be no indication for a vaporization coefficient significantly different from unity.

The partial pressures of U(g), P(g), and P_2(g) were calculated to be 2.58×10^{-6}, 1.89×10^{-6}, and 4.62×10^{-7} atm, respectively, at 2309°K. The equations for the temperature dependencies of the three partial pressures in atmospheres are

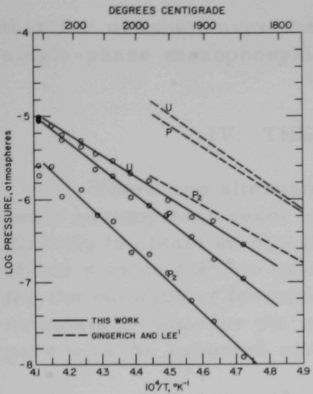
$$\log P_U = (5.677 \pm 0.273) - (25898 \pm 192)/T, \tag{2}$$

$$\log P_P = (8.062 \pm 0.240) - (31831 \pm 340)/T, \tag{3}$$

and

$$\log P_{P_2} = (10.319 \pm 1.203) - (38454 \pm 1480)/T \tag{4}$$

from the four series of ion-current measurements, mentioned previously, which had been combined by normalizing the data to a common basis at the midrange temperature. These equations are considered valid in the range 2073-2423°K. From the uncertainty in the experimental data alone, the partial pressures of U(g), P(g), and P_2(g) are known (at a 95% confidence level, 2σ) to within 18, 20, and 44%, respectively. However, it is generally assumed that uncertainties in the ionization cross sections and multiplier efficiencies could be a factor of two. Figure 1 shows the lines representing the above pressure equations, one set of the experimental data (the previous data is given in Table I, Series A), and, for comparison, the equations reported by Gingerich and Lee[7] from their similar mass-spectrometric

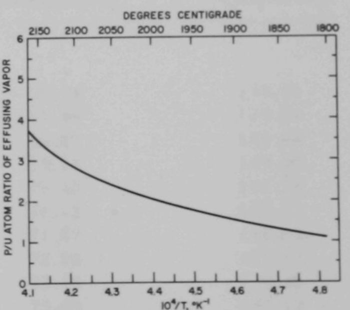


308-1032 Rev. 1

Fig. 1. Mass-spectrometrically Determined Partial Pressures of U(g), P(g), and P_2(g) over the U-UP System

effusion experiments. There is considerable disagreement between their absolute pressures and enthalpies of vaporization and ours. Their partial pressures are approximately an order of magnitude greater than our corresponding pressures. The apparent enthalpies of vaporization that we derive from their vapor-pressure equations (Eqs. 5, 6, and 7 of Ref. 1) are $\overline{\Delta H}(U)$ = 131.2 kcal/mole, $\overline{\Delta H}(P)$ = 120.0 kcal/mole, and $\overline{\Delta H}(P_2)$ = 105.5 kcal/mole, as compared to our values of 118.5, 145.7, and 176.0 kcal/mole from Eqs. 2, 3, and 4, respectively. The internal consistency of our results, as judged by the $P_2 \rightleftharpoons 2P$ equilibrium, was very satisfactory. The Gibbs free energy, enthalpy, and entropy of dissociation of P_2(g), calculated from Eqs. 3 and 4 at 2248°K were 55.6 kcal/mole, 115.4 kcal/mole, and 26.6 eu, respectively. From spectroscopic data,[23] the corresponding values are 54.8 kcal/mole, 119.2 kcal/mole, and 28.7 eu. Also, a comparison at 2309°K of our partial pressure ratios shows a monomer/dimer ratio of 4.09 from direct measurement (using the estimated cross sections and detector efficiencies), versus 4.90 calculated from inserting the measured monomer pressure into the equilibrium constant[23] expression. As mentioned in the Introduction, Gingerich and Lee's P_2 = 2P data[1] did not agree with these well-established equilibrium data,[23] and their suggestion that the discord was probably due "...especially to possible temperature gradients in the effusion cell..." could also serve as a possible explanation for the disagreement between our work and theirs. Another possible explanation could be that their vaporization was from a single condensed phase, in that their UP_{1-x} solid had not changed sufficiently to form the liquid-uranium phase.

The observed change in composition during effusion of stoichiometric uranium monophosphide over to the system of two condensed phases demands that the vapor effusing from the cell be phosphorus-rich. The partial pressure data expressed by Eqs. 2, 3, and 4 are consistent with this requirement. Figure 2 presents the derived atom ratio of the vapor effusing from the two-phase system in the Knudsen cell as a function of temperature. Since the rate of effusion loss of phosphorus substantially exceeds



308-1033

Fig. 2. The P/U Atom Ratio as a Function of Temperature Effusing from a Knudsen Cell Containing U-UP System

effusion experiments. There is considerable disagreement between their absolute pressures and enthalpies of vaporization and ours. Their partial pressures are approximately an order of magnitude greater than our corresponding pressures. The apparent enthalpies of vaporization that we derive from their vapor-pressure equations (Eqs. 5, 6, and 7 of Ref. 11) are $\overline{\Delta H}(U)$ = 131.2 kcal/mole, $\overline{\Delta H}(P)$ = 120.0 kcal/mole, and $\overline{\Delta H}(P_2)$ = 105.5 kcal/mole as compared to our values of 118.5, 145.7, and 176.0 kcal/mole from Eqs. 2, 3, and 4, respectively. The internal consistency of our results, as judged by the $P_2 = 2P$ equilibrium, was very satisfactory. The Gibbs free energy, enthalpy, and entropy of dissociation of $P_2(g)$ calculated from Eqs. 3 and 4 at 2248°K were 55.0 kcal/mole, 115.4 kcal/mole, and 26.8 eu, respectively. From spectroscopic data,[23] the corresponding values are 54.8 kcal/mole, 119.2 kcal/mole, and 28.7 eu. Also, a comparison at 2309°K of our partial pressure ratios shows a monomer/dimer ratio of 4.09 from direct measurement (using the estimated cross sections and detector efficiencies), versus 4.90 calculated from inserting the measured monomer pressure into the equilibrium constant[23] expression. As mentioned in the Introduction, Gingerich and Lee's $P_2 = 2P$ data[11] did not agree with these well-established equilibrium data,[23] and their suggestion that the discord was probably due "...especially to possible temperature gradients in the effusion cell..." could also serve as a possible explanation for the disagreement between our work and theirs. Another possible explanation could be that their vaporization was from a single condensed phase in that their UP_{1-x} solid had not changed sufficiently to form the liquid-uranium phase.

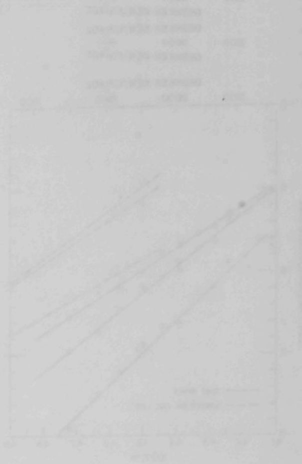


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Fig. 1. Mass-Spectrometrically Determined Partial Pressures of U(g), P(g), and P_2(g) over the U-UP System

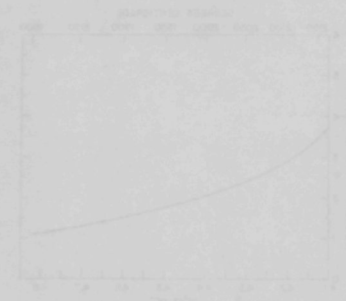

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Fig. 2. The P/U Atom Ratio as a Function of Temperature Effusing from a Knudsen Cell Containing U-UP System

The observed change in composition during effusion of stoichiometric uranium monophosphide over to the system of two condensed phases demands that the vapor effusing from the cell be phosphorus-rich. The partial pressure data expressed by Eqs. 2, 3, and 4 are consistent with this requirement. Figure 2 presents the derived atom ratio of the vapor effusing from the two-phase system in the Knudsen cell as a function of temperature. Since the rate of effusion loss of phosphorus substantially exceeds that for uranium over the two-phase system, it must be true for the single-phase monophosphide also.

IV. THERMODYNAMIC EVALUATIONS

There are alternate ways of treating our data, depending upon which basic assumptions seem most reliable. One may treat the uranium data directly to obtain an enthalpy of sublimation of uranium. One may also obtain a value for this quantity indirectly by using calorimetric data reported for the enthalpy of formation of UP(s). The third possibility, of course, is to calculate a value for the enthalpy of formation of UP from our data to compare with the reported value. These alternatives are considered below.

A. Direct Calculation of the Enthalpy of Vaporization and Sublimation of Uranium

If we assume that the liquid uranium of the two-phase system, saturated with $UP_{1-x_s}(s)$ and W(s), is at unit activity at all temperatures of the measurements, the partial uranium pressures, expressed by Eq. 2, would represent the true vapor pressure of liquid uranium, and the second-law apparent partial enthalpy, 118.5 ± 0.9 kcal/mole at 2248°K, would be the enthalpy of vaporization of uranium. This value, calculated to 298°K through use of the Hultgren et al.[24] functions, yields ΔH°_{298} = 128.3 ± 1.3 kcal/mole for the enthalpy of sublimation of uranium. Table I lists the primary log P_U data and the derived third-law enthalpies of sublimation for the

TABLE I. Third-law Determinations of the Enthalpy of Sublimation of Uranium at 298°C

Temp (°K)	-Log P_U (atm)	ΔG°_T (kcal/mole)	$-\Delta(G^\circ_T - H^\circ_{298})^a$ (kcal/mole)	$\Delta H^\circ_{298}(U)$ (kcal/mole)
		Series A		
2118	6.546	65.21	66.14	131.35
2158	6.262	61.84	67.20	129.04
2223	6.007	61.09	68.87	129.96
2251	5.766	59.39	69.61	129.00
2280	5.689	59.34	70.40	129.74
2307	5.525	58.38	71.15	129.53
2335	5.446	58.16	71.87	130.03
2358	5.294	57.12	72.50	129.62
2390	5.220	57.11	73.35	130.46
2408	5.106	56.27	73.85	130.12
2430	5.002	55.62	74.42	130.04
2430	5.007	55.68	74.42	130.10

TABLE I (Contd.)

Temp (°K)	$-\log P_U$ (atm)	ΔG°_T (kcal/mole)	$-\Delta(G^\circ_T - H^\circ_{298})$[a] (kcal/mole)	$\Delta H^\circ_{298}(U)$ (kcal/mole)
		Series B		
2112	6.590	63.69	65.97	129.66
2112	6.590	63.69	65.97	129.66
2112	6.596	63.75	65.97	129.72
2146	6.381	62.66	66.87	129.53
2146	6.373	62.58	66.87	129.45
2147	6.394	62.82	66.89	129.71
2178	6.217	61.96	67.70	129.66
2178	6.238	62.17	67.70	129.87
2237	5.868	60.09	69.25	129.34
2237	5.899	60.41	69.25	129.66
2240	5.921	60.69	69.33	130.02
2268	5.746	59.64	70.10	129.74
2268	5.763	59.82	70.10	129.92
2270	5.743	59.67	70.12	129.79
2270	5.759	59.84	70.12	129.96
2344	5.388	57.81	72.10	129.91
2345	5.370	57.62	72.13	129.75
2370	5.194	56.35	72.81	129.16
2370	5.217	56.60	72.81	129.41
2370	5.223	56.67	72.81	129.48
2372	5.210	56.53	72.85	129.38
2380	5.183	56.44	73.09	129.53
2382	5.191	56.58	73.13	129.71
2410	5.053	55.73	73.88	129.61
2410	5.082	56.05	73.88	129.93
2410	5.044	55.64	73.88	129.52
		Series C		
2126	6.464	62.89	66.35	129.24
2126	6.354	61.82	66.35	128.17
2126	6.514	63.37	66.35	129.72
2229	5.965	60.84	69.05	129.89
2229	5.968	60.87	69.05	129.92
2229	5.947	60.66	69.05	129.71
2284	5.676	59.31	70.51	129.82
2284	5.670	59.25	70.51	129.76
2284	5.706	59.63	70.51	130.14
2284	5.680	59.36	70.51	129.87
2344	5.342	57.32	72.10	129.42
2344	5.379	57.72	72.10	129.82
2344	5.359	57.50	72.10	129.60
2391	5.164	56.49	73.39	129.88
2391	5.169	56.55	73.39	129.94
2391	5.164	56.49	73.39	129.88

TABLE I (Contd.)

Temp (°K)	-Log P_U (atm)	ΔG°_T (kcal/mole)	$-\Delta(G^\circ_T - H^\circ_{298})$[a] (kcal/mole)	$\Delta H^\circ_{298}(U)$ (kcal/mole)
		Series D		
2073	6.805	64.55	64.94	129.49
2073	6.859	65.06	64.94	130.00
2073	6.793	64.44	64.94	129.38
2145	6.390	62.72	66.85	129.57
2147	6.403	62.91	66.89	129.80
2147	6.370	62.59	66.89	129.48
2148	6.382	62.73	66.92	129.65
2189	6.212	62.24	68.00	130.24
2209	6.049	61.16	68.51	129.67
2209	6.037	61.03	68.51	129.54
2210	6.080	61.47	68.54	130.01
2210	6.041	61.07	68.54	129.61
2210	6.112	61.79	68.54	130.33
2270	5.739	59.63	70.12	129.75
2270	5.733	59.57	70.12	129.69
2270	5.769	59.94	70.12	130.06
2270	5.755	59.79	70.12	129.91
2324	5.482	58.27	71.56	129.83
2326	5.436	57.84	71.65	129.49
2326	5.461	58.11	71.65	129.76
2326	5.461	58.11	71.65	129.76
2326	5.472	58.22	71.65	129.87
2378	5.159	56.13	73.05	129.18
2378	5.166	56.21	73.05	129.26
2389	5.075	55.47	73.32	128.79
			Av. = 129.7 ± 0.4[b]	

[a]Values taken from a smooth curve drawn through the listed values compiled by Hultgren et al.[24]

[b]This standard deviation reflects the precision. The accuracy of the value is estimated to be ±3.3 kcal/mole.

four series of measurements. The values do not show a temperature trend, and the average value, ΔH°_{298} = 129.7 ± 3.3 kcal/mole, is in satisfactory agreement with the second-law value. The average of the second- and third-law values is 129.0 ± 3.7 kcal/mole.

B. Indirect Calculation of the Enthalpy of Sublimation of Uranium

Here, we first assume that the enthalpies derived from Eqs. 2 and 3 are valid partial molar values for any of the compositions UP_{1-x_s}, where x_s refers to the uranium saturation boundary. This could be true if x_s did not vary significantly with temperature or if the partial pressures at each temperature did not vary significantly in the range of variation of x_s. Then

it would follow that the "apparent" partial molar enthalpies obtained for the two-phase preparations, from Eqs. 2 and 3, would be valid partial molar quantities and constant in the range of variation of x_s. A second assumption required regards the variation of these partial molar enthalpies for the range x_s to $x = 0$. It is assumed that the variation is negligible or that the change in the partial enthalpy for one component compensates for the change in the other component (as they would at least tend to do). Subject to these assumptions, the enthalpy of sublimation of $UP_{1.00}(s)$ to the monatomic gases is the sum of their partial molar enthalpies of vaporization or 264.2 ± 1.8 kcal/mole. Using this data, one can calculate an enthalpy of sublimation (in kcal/mole) for uranium at 298°K from the following cycle:

$UP_{1.00}(s,2248) = U(g,2248) + P(g,2248)$	$\Delta H = 264.2 \pm 1.8$
$UP_{1.00}(s,298) = UP_{1.00}(s,2248)$	$\Delta H = 26.9 \pm 1.6$*
$P(g,2248) = P(g,298)$	$\Delta H = -9.8 \pm 0.1$ (Ref. 23)
$P(g,298) = P(red,298)$	$\Delta H = -79.8 \pm 0.6$ (Ref. 23)
$P(red,298) = P(\alpha,298)$	$\Delta H = 3.9 \pm 0.8$ (Ref. 26)
$U(g,2248) = U(g,298)$	$\Delta H = -12.7 \pm 1.3$ (Ref. 24)
$P(\alpha,298) + U(\alpha,298) = UP_{1.00}(s,298)$	$\Delta H = -75.5 \pm 0.7$ (Ref. 27)
$U(\alpha,298) = U(g,298)$	$\Delta H = 117.2 \pm 3.0$

The value derived for the enthalpy of sublimation, 117.2 ± 3.0 kcal/mole, is essentially a second-law value.

C. Calculation of a Value for the Enthalpy of Formation of $UP_{1.00}(s)$

The most obvious way to calculate an enthalpy of formation from our high-temperature equilibrium data is to use the thermodynamic cycle given above and solve for the enthalpy of formation of $UP_{1.00}$ rather than the enthalpy of sublimation of U(g). If one does this, using the average value of our second- and third-law determinations for the enthalpy of sublimation of U(g) at 298°K, 129.0 ± 3.7 kcal/mole, an enthalpy of formation for $UP_{1.00}$ at 298°K is calculated to be -63.7 ± 4.4 kcal/mole. A third-law evaluation gives the same result within 1.8 kcal/mole. To eliminate the necessity of using an enthalpy of sublimation for U(g), we could have used a thermodynamic cycle based on our data for the following reaction:

$$U(\ell) + (1 - x)\, P(g) = UP_{1-x}(s). \tag{5}$$

Here we would again assume not only that the liquid uranium of the two-phase equilibria is at unit activity in the temperature range of the

*Calculated using the reported mean heat capacity for uranium monophosphide, 13.8 cal/deg/mole, in the range 1073-1473°K by Brugger.[25]

It would follow that the "apparent" partial molar enthalpies obtained for the two-phase preparations, from Eqs. 2 and 3, would be valid partial molar quantities and constant in the range of variation of x_s. A second assumption required regards the variation of these partial molar enthalpies for the range x_s to $x = 0$. It is assumed that the variation is negligible or that the change in the partial enthalpy for one component compensates for the change in the other component (as they would at least tend to do). Subject to these assumptions, the enthalpy of sublimation of $UP_{1.00}(s)$ to the monatomic gases is the sum of their partial molar enthalpies of vaporization or 264.2 ± 1.8 kcal/mole. Using this data, one can calculate an enthalpy of sublimation (in kcal/mole) for uranium at 298°K from the following cycle

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$$U(\ell) + (1 - x)\,P(g) = UP_{1-x}(s). \qquad (5)$$

Here we would again assume not only that the liquid uranium of the two-phase equilibria is at unit activity in the temperature range of the

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*Calculated using the reported mean heat capacity for uranium monophosphide, 14.8 cal/deg/mole, in the range 1043-1472°K by Rugger.[25]

measurements, but also that the activity of UP_{1-x} is not significantly different from unity over the temperature range of measurements. With these assumptions, the second-law enthalpy of formation for Reaction 5 is simply -145.7 kcal/mole from Eq. 3. If this value is corrected from the midrange temperature, 2248 to 298°K, using the appropriate thermodynamic functions listed in the references given in the cycle above, a value for the enthalpy of formation of $UP_{1.00}$ identical to the one calculated above is obtained.

V. DISCUSSION

Let us first consider our direct calculation of the enthalpy of sublimation of uranium. The question of the correct value for this quantity has recently been reviewed by Ackermann and Rauh,[28] who also present new data concerning the effect of dissolved tantalum, phosphorus, sulfur, carbon, and oxygen on the vapor pressure of liquid uranium. They noted the substantial agreement between our second-law enthalpy of vaporization for uranium over the $U(\ell)$-$UP_{1-x}(s)$ system (118.5 ± 0.9 kcal/mole at 2248°K) and their result (115.5 ± 1.7 kcal/mole at 2100°K). They found that uranium phosphide had the smallest effect of any of the compounds on the vapor pressure of uranium and estimated an activity of ~0.9 at 2000°K, which adequately supports our assumption of unit activity in our calculations. Although our uranium partial pressures are in close agreement with those of Pattoret _et al_.,[29] for uranium in a tungsten or tantalum effusion cell (2.89×10^{-6} atm of 2309°K compared to their 4.15×10^{-6} atm), they are a factor of approximately one-half lower than those obtained by Ackermann and Rauh.[28] The latter authors' suggestion, that our values are low because of the rate-of-mass-loss method of calibration with its usual failure[30] to account for nonideal cosine distribution of the effusing molecules, seems reasonable.

Ackermann and Rauh[28] evaluated an enthalpy of sublimation for uranium at 298°K of 126.3 ± 1.0 kcal/mole and compared it with 128.5 ± 2.0 kcal/mole by Pattoret _et al_.[29] (this value being actually for 0°K) and 123.7 ± 1.3 kcal/mole reported by Leitnaker and Godfrey.[31]

Both our second-law (128.3 ± 1.3) and our third-law (129.7 ± 3.3) values and their average (129.0 ± 3.7) are in excellent agreement with the values reported by Pattoret _et al_.[29] and Ackermann and Rauh.[28] Our results thus support the long-held contention of the former authors and the more recently expressed view of the latter that the earlier value of Rauh and Thorn,[32] 116.6 kcal/mole, is no longer tenable.

Our indirect calculation of the enthalpy of sublimation of uranium, using the enthalpy of formation of UP by O'Hare _et al_.[27] and yielding a value of 117.2 kcal/mole, points up an inconsistency in this calculation. Likewise, measurements, but also that the activity of UP_{1-x} is not significantly different from unity over the temperature range of measurements. With these assumptions, the second-law enthalpy of formation for Reaction 5 is simply -145.7 kcal/mole from Eq. 3. If this value is corrected from the midrange temperature, 2248 to 298°K, using the appropriate thermodynamic functions listed in the references given in the cycle above, a value for the enthalpy of formation of $UP_{1.00}$ identical to the one calculated above is obtained.

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Our indirect calculation of the enthalpy of sublimation of uranium, using the enthalpy of formation of UP by O'Hare et al.[33] and yielding a value of 117.2 kcal/mole, points up an inconsistency in this calculation. Likewise this inconsistency is seen in our value for the enthalpy of formation for $UP_{1.00}$ at 298°K of -63.7 ± 4.4 kcal/mole compared to the calorimetric value of -75.5 ± 0.7 kcal/mole of O'Hare et al. Since there seems little reason to suspect the calorimetric value for the enthalpy, doubt is cast on one or both of the assumptions used in our calculations. Most likely one cannot assume that the partial molar enthalpies of vaporization of U(g) and P(g) are constant over the composition range of UP_{1-x} to $UP_{1.00}$.

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